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Hong et al.

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(54) **ACYCLIC CARBENE LIGAND FOR RUTHENIUM COMPLEX FORMATION, RUTHENIUM COMPLEX CATALYST, AND USE THEREOF**

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C07D 211/70 (2013.01); *C07F 15/0046*
(2013.01); *B01J 2231/48* (2013.01); *B01J 2231/543* (2013.01); *B01J 2531/004* (2013.01);
B01J 2531/821 (2013.01); *C07C 2531/12*
(2013.01)

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(58) **Field of Classification Search**
None
See application file for complete search history.

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(56) **References Cited**

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FOREIGN PATENT DOCUMENTS

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 175 days.

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(21) Appl. No.: **17/091,669**

Koganty et al. "Reactions of acid halides and chloroformates involving an intermediate with dimethylformamide" *Tetrahedron Letters*, 1973, vol. 14, No. 45, pp. 4511-4514.*

(22) Filed: **Nov. 6, 2020**

* cited by examiner

(65) **Prior Publication Data**

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(57) **ABSTRACT**

(51) **Int. Cl.**

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C07F 15/00 (2006.01)
C07C 6/04 (2006.01)
C07C 251/30 (2006.01)

Provided are a novel acyclic carbene ligand for ruthenium complex formation; a ruthenium complex catalyst using the ligand; a method of using the complex as a catalyst in an ethylene-metathesis ethenolysis reaction; a method of preparing the ruthenium complex catalyst; and a method of preparing a linear alpha-olefin, the method including the step of reacting a linear or cyclic alkene compound in the presence of the ruthenium complex catalyst.

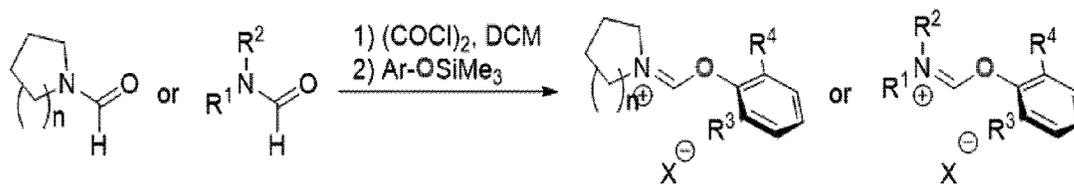
The acyclic carbene ligand of the present invention and the ruthenium complex catalyst using the same have high selectivity and turnover number for terminal olefin formation in an ethylene-metathesis ethenolysis reaction, and thus linear α -olefins may be prepared with a high yield.

(52) **U.S. Cl.**

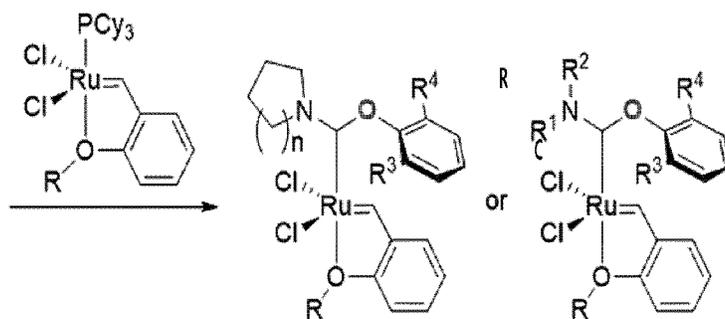
CPC *B01J 31/2278* (2013.01); *B01J 31/2226* (2013.01); *B01J 37/04* (2013.01); *C07C 6/04* (2013.01); *C07C 251/30* (2013.01); *C07D*

11 Claims, 2 Drawing Sheets

FIG. 1



L1 - L12



Ru1 - Ru14

FIG. 2A

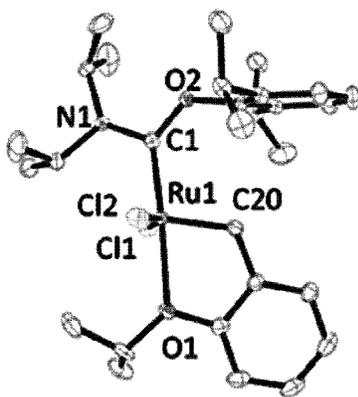


FIG. 2B

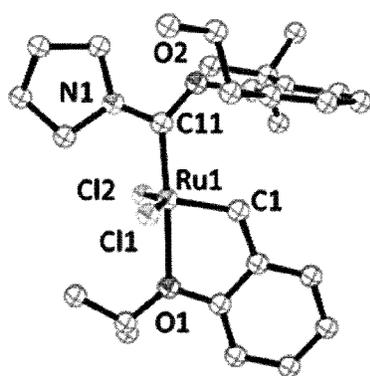
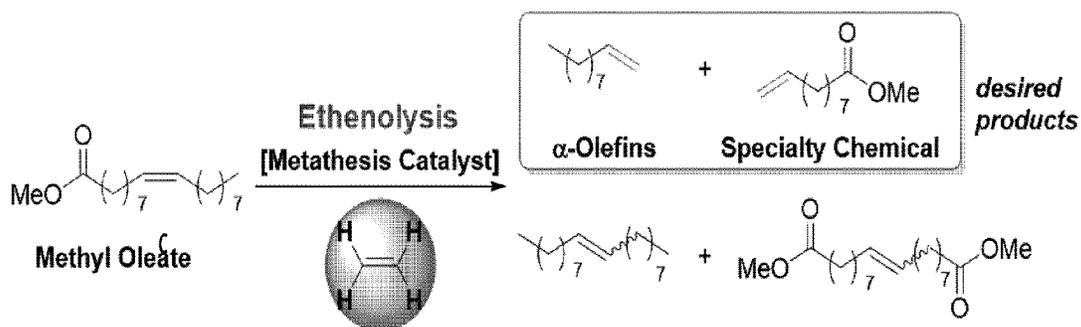


FIG. 3



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**ACYCLIC CARBENE LIGAND FOR
RUTHENIUM COMPLEX FORMATION,
RUTHENIUM COMPLEX CATALYST, AND
USE THEREOF**

CROSS-REFERENCE TO RELATED
APPLICATION

This application claims priority under 35 U.S.C. § 119 to Korean Patent Application No. 10-2019-0142835, filed on Nov. 8, 2019 in the Korean Intellectual Property Office (KIPO), the contents of which are herein incorporated by reference in their entirety.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a novel, acyclic carbene ligand for ruthenium complex formation; a ruthenium complex catalyst using the ligand; a method of using the complex as a catalyst in an ethylene-metathesis ethenolysis reaction; a method of preparing the ruthenium complex catalyst; and a method of preparing a linear α -olefin, the method including the step of reacting a linear or cyclic alkene compound in the presence of the ruthenium complex catalyst.

2. Description of the Related Art

Known since 1977, the Shell Higher Olefin Process (SHOP) is a method of synthesizing linear α -olefins obtained from petrochemical raw materials. The Shell Higher Olefin Process has a problem in that linear α -olefins have a wide distribution, with 41% of linear α -olefins having 4 to 8 carbon atoms, 40.5% of linear α -olefins having 10 to 18 carbon atoms, and 18.5% of linear α -olefins having 20 or more carbon atoms. For example, the Snell Higher Olefin Process has a problem of a low synthesis yield of 1-decene. In addition, this method requires a high temperature of 60° C. to 300° C. and a high pressure of 30 bar to 200 bar.

In one aspect to solve these problems, research, and development are actively being conducted on ruthenium complex catalysts for olefin metathesis. The Grubbs catalyst, awarded the Nobel Prize in Chemistry in 2005, is known as a ruthenium complex catalyst.

Meanwhile, for the preparation of linear α -olefins, natural seed oil may be used instead of petroleum raw materials. For example, a method of synthesizing linear α -olefins from renewable seed oil as a raw material is as follows. Cross-metathesis of methyl oleate with ethylene may be performed. C=C double bonds are decomposed by ethenolysis of methyl oleate. Accordingly, it is possible to synthesize a desired linear α -olefin. Unlike the Shell Higher Olefin Process described above, the synthesis yield of a single 1-decene is high. In addition, unlike the Shell Higher Olefin Process described above, cross-metathesis using a Ru catalyst is advantageous in that it may be performed at a low temperature of 40° C. to 100° C. and at a low pressure of about 10 bar.

Further, a ruthenium complex catalyst having a N heterocyclic carbene (NHC) ligand, is known. The ruthenium

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complex having an asymmetrically substituted N-heterocyclic carbene ligand exhibits high selectivity for cross-metathesis products over self-metathesis by-products, and thus if has been identified as a promising catalyst for ethenolysis. Stabilization of a methyldene intermediate has been suggested as a key factor in enhancing catalytic activity.

An additional electron-donating ligand is known to help stabilize the methyldene intermediate, but there is a problem in that a phosphine ligand undergoes decomposition by way of phosphine.

Meanwhile, imidazo [1,5-a]pyridine-3-ylidene (ImPy) which was first reported in 2005 is a candidate for the structurally asymmetric NRC ligand and has various electronic properties.

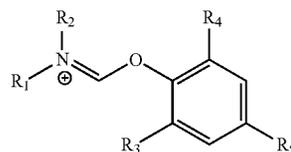
However, the above catalysts still have low selectivity for the formation of terminal olefins, and thus there is a need for the development of a new catalyst. In addition, a catalyst using a cyclic carbene ligand is known (Korean Patent Application No. 10-2019-7026049), but there has been no report regarding a ruthenium catalyst using an acyclic carbene ligand as in the present invention.

Accordingly, the present inventors have developed a novel acyclic aminooxycarbene ligand having high catalytic activity, high selectivity for the formation of terminal olefins in ethenolysis of methyl oleate, and high stability, thereby completing a ruthenium complex ligand and a ruthenium complex.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an acyclic carbene ligand for the formation of a ruthenium complex, the acyclic carbene ligand having a structure of the following Chemical Formula 1:

[Chemical Formula 1]



wherein, in Chemical Formula 1,

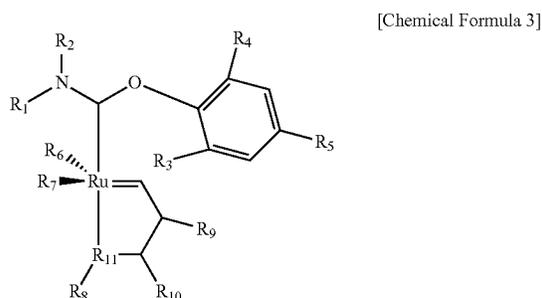
R₁ and R₂ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group; or R₁ and R₂ are connected to each other to form an unsubstituted or substituted 4- to 8-membered heterocycle with a nitrogen atom to which they are connected,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group, and

R₅ is a hydrogen atom or C₁-C₆ alkyl group.

Another object of the present invention is to provide a ruthenium complex catalyst having a structure of the following Chemical Formula 3:

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wherein, in Chemical Formula 3,

R₁ and R₂ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group; or R₁ and R₂ are connected to each other to form an unsubstituted or substituted 4- to 8-membered heterocycle with a nitrogen atom to which they are connected,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group,

R₅ is a hydrogen atom or C₁-C₆ alkyl group,

R₆ and R₇ are each independently a halogen,

R₈ is a substituted or unsubstituted C₁-C₁₀ alkyl group, C₅-C₁₀ carbocycle, or 5- to 10-membered heterocycle,

R₉ and R₁₀ are each independently a C₁-C₁₀ alkyl group, or are connected to each other to form a C₅-C₁₀ carbocycle or a 5- to 10-membered heterocycle, and

R₁₁ is N or O.

Still another object of the present invention is to provide a method of using the ruthenium complex as a catalyst in ethylene-metathesis ethenolysis of a linear or cyclic alkene compound.

Still another object of the present invention is to provide a method of preparing a ruthenium complex catalyst, the method including the steps of treating formamide with oxalyl chloride ((COCl)₂) to obtain an intermediate; reacting the intermediate with alkoxy silane (RORMS) to obtain an acyclic carbene ligand having a structure of Chemical Formula 1; and binding the ligand with ruthenium (Ru) to form a ruthenium complex catalyst having a structure of Chemical Formula 4.

Still another object of the present invention is to provide a method of preparing a linear alpha-olefin (linear α -olefin), the method including the step of reacting a linear or cyclic alkene compound in the presence of the ruthenium complex catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates an acyclic carbene ligand and a reaction scheme for producing a ruthenium complex catalyst using the same;

FIG. 2A shows the result of X-ray crystal analysis of a ruthenium complex catalyst;

FIG. 2B shows the result of X-ray crystal analysis of a ruthenium complex catalyst; and

FIG. 3 shows ethenolysis of methyl oleate as a specific exemplary embodiment of ethenolysis.

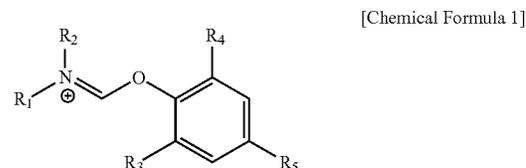
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the present invention will be described in detail. Meanwhile, each description and embodiment dis-

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closed in this disclosure may also be applied to other descriptions and embodiments. That is, all combinations of various elements disclosed in this disclosure fall within the scope of the present invention. Further, the scope of the present invention is not limited by the specific description described below.

To achieve the above object, an aspect of the present invention provides an acyclic carbene ligand for the formation of a ruthenium (Ru) complex, the acyclic carbene ligand having a structure of the following Chemical Formula 1:



wherein, in Chemical Formula 1,

R₁ and R₂ are each independently a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group; or R₁ and R₂ are connected to each other to form an unsubstituted or substituted heterocycle with a nitrogen atom to which they are connected,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted alkyl group, alkenyl group, alkynyl group, a substituted or unsubstituted cycloalkyl group, or a substituted or unsubstituted aryl group, and

R₅ is a hydrogen atom or alkyl group.

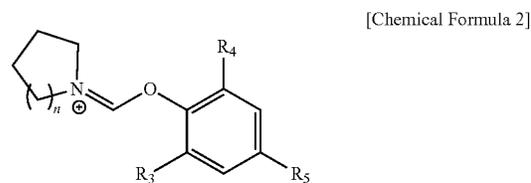
More specifically, the acyclic carbene ligand, for the formation of the ruthenium complex has the structure of Chemical Formula 1,

wherein R₁ and R₂ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group; or R₁ and R₂ are connected to each other to form an unsubstituted or substituted 4- to 8-membered heterocycle with a nitrogen atom to which they are connected,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group, and

R₅ is a hydrogen atom or C₁-C₆ alkyl group.

The acyclic carbene ligand for the formation of the ruthenium complex may have a structure of the following Chemical Formula 2:



wherein, in Chemical Formula 2,

n is an integer of 0 or more,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted alkyl group, alkenyl group, alkynyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, and

R₅ is a hydrogen atom or alkyl group.

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More specifically, the acyclic carbene ligand for the formation of the ruthenium complex has the structure of Chemical Formula 2,

wherein n is an integer of 0 to 4,

R_3 and R_4 are each independently a hydrogen atom, a substituted or unsubstituted C_1 - C_6 alkyl group, C_1 - C_6 alkenyl group, C_1 - C_6 alkynyl group, C_3 - C_8 cycloalkyl group, or C_6 - C_{10} aryl group, and

R_5 is a hydrogen atom or C_1 - C_6 alkyl group.

Further, specifically, the acyclic carbene ligand for the formation of the ruthenium complex has the structure of Chemical Formula 2,

wherein n is an integer of 1 or 2, and

R_3 and R_4 may be propyl, butyl, or diphenylmethyl, but are not limited thereto.

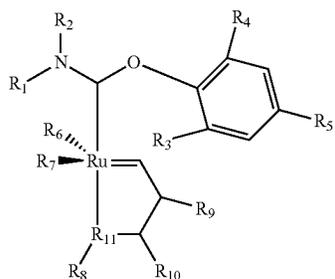
As used herein, the term “acyclic carbene ligand (acyclic aminoxy carbene)” or “carbene ligand” refers to a compound having a structure in which $N-C-O$ is connected in an acyclic form, and is a novel carbene ligand which has not been disclosed. The acyclic carbene ligand forms a complex with ruthenium to be used as a catalyst in ethylene-metathesis ethenolysis, and this use was also first identified in the present invention.

Specifically, the acyclic carbene ligand has high selectivity and turnover, as compared with a cyclic carbene ligand or a $N-C-N$ acyclic carbene (acyclic diamino carbene) ligand, and can thereby prepare linear alpha-olefins with high yield.

The term “selectivity” may mean that cross-metathesis products are produced in a high ratio, as compared with self-metathesis by-products, in the ethylene-metathesis ethenolysis, and in particular, terminal olefins are produced in a high ratio, but the term is not limited thereto.

In one exemplary embodiment of the present invention, it was confirmed that when ethenolysis is performed using the ruthenium complex catalyst having the acyclic carbene ligand of the present invention, the yield of linear alpha-olefins may be increased due to high selectivity.

To achieve the above object, another aspect of the present invention provides a ruthenium complex catalyst having a structure of the following Chemical Formula 3, the ruthenium complex catalyst using the acyclic carbene ligand:



[Chemical Formula 3]

wherein, in Chemical Formula 3,

R_1 and R_2 are each independently a hydrogen atom, a substituted or unsubstituted C_1 - C_6 alkyl group, C_3 - C_8 cycloalkyl group, or C_6 - C_{10} aryl group; or R_1 and R_2 are

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connected to each other to form an unsubstituted or substituted 4- to 8-membered heterocycle with a nitrogen atom to which they are connected,

R_3 and R_4 are each independently a hydrogen atom, a substituted or unsubstituted C_1 - C_6 alkyl group, C_1 - C_6 alkenyl group, C_1 - C_6 alkynyl group, C_3 - C_8 cycloalkyl group, or C_6 - C_{10} aryl group,

R_5 is a hydrogen atom or C_1 - C_6 alkyl group,

R_6 and R_7 are each independently a halogen,

R_8 is a substituted or unsubstituted C_1 - C_{10} alkyl group, C_6 - C_{10} carbocycle, or 5- to 10-membered heterocycle,

R_9 and R_{10} are each independently a C_1 - C_{10} alkyl group, or are connected with each other to form a C_5 - C_{10} carbocycle or a 5- to 10-membered heterocycle, and

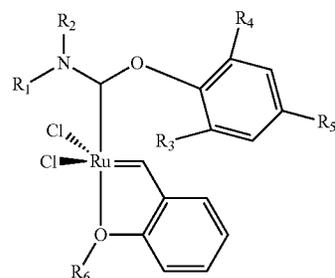
R_{11} is N or O.

Specifically, the alkyl and alkoxy are each independently substituted or unsubstituted with at least one of a halogen, hydroxyl, and amino group;

the carbocycle and heterocycle are each independently a saturated or unsaturated ring of a single or double ring, which is substituted or unsubstituted with at least one selected from the group consisting of a halogen, a nitro group, a C_1 - C_5 alkyl group, a halo (C_1 - C_5 alkyl) group, a C_1 - C_5 alkoxy group, and a phenyl group; and

the heterocycle includes at least one heteroatom selected from N, S, and O.

To achieve the above object, still another aspect of the present invention provides a ruthenium complex catalyst having a structure of the following Chemical Formula 4, the ruthenium complex catalyst using the acyclic carbene ligand:



[Chemical Formula 4]

wherein, in Chemical Formula 4,

R_1 and R_2 are each independently a hydrogen atom, a substituted or unsubstituted C_1 - C_6 alkyl group, C_3 - C_8 cycloalkyl group, or C_6 - C_{10} aryl group; or R_1 and R_2 are connected to each other to form an unsubstituted or substituted 4- to 8-membered heterocycle with a nitrogen atom to which they are connected,

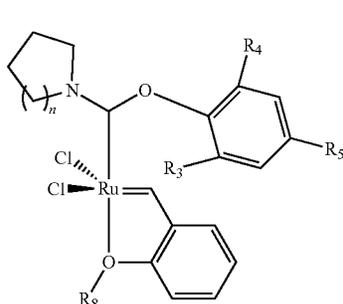
R_3 and R_4 are each independently a hydrogen atom, a substituted or unsubstituted C_1 - C_6 alkyl group, C_1 - C_6 alkenyl group, C_1 - C_6 alkynyl group, C_3 - C_8 cycloalkyl group, or C_6 - C_{10} aryl group,

R_5 is a hydrogen atom or C_1 - C_6 alkyl group, and

R_8 is a substituted or unsubstituted C_1 - C_{10} alkyl group, C_5 - C_{10} carbocycle, or 5- to 10-membered heterocycle.

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The ruthenium complex catalyst may have a structure of the following Chemical Formula 5:



[Chemical Formula 5]

wherein, in Chemical Formula 5,
n is an integer of 0 to 4,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group,

R₅ is a hydrogen atom or C₁-C₆ alkyl group, and

R₈ is a substituted or unsubstituted C₁-C₁₀ alkyl group, C₅-C₁₀ carbocycle, or 5- to 10-membered heterocycle.

Specifically, the ruthenium complex catalyst has the structure of Chemical Formula 5,

wherein n is an integer of 1 or 2, and

R₃ and R₄ may be propyl, butyl, or diphenylmethyl, but is not limited thereto.

As used herein, the term "ruthenium complex catalyst" or "ruthenium catalyst" may mean that the acyclic carbene ligand and ruthenium (Ru) metal produce a complex (a complex compound) to be used as a catalyst in the ethylene-metathesis ethenolysis reaction.

In one exemplary embodiment of the present invention, it was confirmed that when the unsubstituted or substituted 4- to 8-membered heterocycle is formed with a nitrogen atom in the structure of Chemical Formula 4 of the ruthenium complex catalyst, the selectivity is increased, and in particular, when a 5- or 6 membered heterocycle including the nitrogen atom is formed, corresponding to the case where n is an integer of 1 or

In this regard, the "ethenolysis reaction", which is a metathesis reaction using ethylene, may mean a reaction that breaks internal olefins to convert them into terminal olefins. Specifically, the ethenolysis reaction may refer to a method of preparing an alpha-linear olefin by using a linear or cyclic alkene compound as a reactant, but is not limited thereto. A specific example of the ethenolysis reaction is an ethenolysis reaction of methyl oleate, as illustrated in FIG. 3.

The ethenolysis reaction has been suggested as a new method of preparing linear alpha-olefins from oils existing in nature, not through a petrochemical process.

In addition, according to recent studies, a ruthenium complex having a N-heterocyclic carbene (NHC) ligand has been studied as one of the catalysts for ethenolysis, but it still has higher selectivity for desired linear α -olefins than self-metathesis by-products, and there is still a need for the development of catalysts to improve reaction efficiency.

In one exemplary embodiment of the present invention, it high selectivity and reaction efficiency are achieved in the production of linear alpha-olefins via the ethenolysis reaction.

As used herein, the term "linear olefin" or "alpha-olefin" or "linear alpha-olefin (linear α -olefin)", which is a product

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of the ethenolysis reaction, may specifically refer to an olefin having a Chemical Formula of C_xH_{2x}.

Specifically, the linear alpha-olefin may include 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and C₂₀-C₂₄, C₂₄-C₃₀, and C₂₀-C₃₀ olefins, but is not limited thereto.

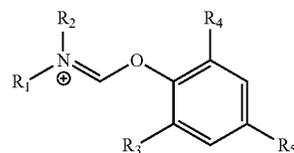
The linear alpha-olefin may be used as a very useful intermediate in the production of detergents, synthetic lubricants, copolymers, plasticizers, and many other important products.

To achieve the above object, still another aspect of the present invention provides a method of using the ruthenium complex as a catalyst in the ethylene-metathesis ethenolysis reaction of a linear or cyclic alkene compound.

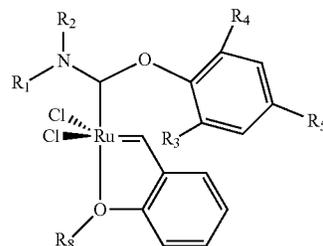
In this regard, the term "ruthenium complex" and "ethenolysis" are the same as described above.

A specific example of the ethylene-metathesis ethenolysis reaction is an ethenolysis reaction of methyl oleate, as illustrated in FIG. 3, and any example may be included, as long as it is the ethenolysis reaction, but the reaction is not limited thereto.

To achieve the above object, still another aspect of the present invention provides a method of preparing the ruthenium complex catalyst, the method including the steps of: treating formamide with oxalyl chloride ((COCl)₂) to obtain an intermediate; reacting the intermediate with alkoxy-silane (ROTMS) to obtain an acyclic carbene ligand having the structure of Chemical Formula 1; and binding the ligand with ruthenium (Ru) to form a ruthenium complex catalyst having the structure of Chemical Formula 4:



[Chemical Formula 1]



[Chemical Formula 4]

wherein, in the above Chemical Formulae,

R₁ and R₂ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group; or R₁ and R₂ are connected to each other to form an unsubstituted or substituted 4- to 8-membered heterocycle with a nitrogen atom to which they are connected,

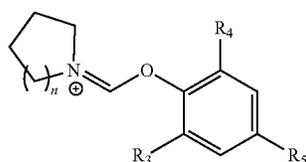
R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group,

R₅ is a hydrogen atom or C₁-C₆ alkyl group, and R₈ is a substituted or unsubstituted C₁-C₁₀ alkyl group, C₅-C₁₀ carbocycle, or 5- to 10-membered heterocycle.

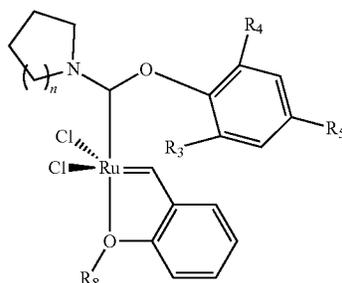
Specifically, the step of obtaining the ligand may be a step of obtaining an acyclic carbene ligand having a structure of Chemical Formula 2,

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and the step of forming the ruthenium complex catalyst may be a step of forming a ruthenium complex catalyst having a structure of Chemical Formula 5:



[Chemical Formula 2]



[Chemical Formula 5]

wherein, in the above Chemical Formulae,
n is an integer of 0 to 4,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group,

R₅ is a hydrogen atom or C₁-C₆ alkyl group, and

R₈ is a substituted or unsubstituted C₁-C₁₀ alkyl, C₅-C₁₀ carbocycle, or 5- to 10-membered heterocycle.

Specifically, the step of binding the ligand with ruthenium to form the ruthenium complex catalyst may be a step of preparing the ruthenium complex catalyst via a phosphine exchange reaction with a phosphine ruthenium catalyst, but is not limited thereto.

The acyclic carbene ligand and the ruthenium complex catalyst are the same as described above.

The intermediate produced by treating formamide with oxalyl chloride ((COCl)₂) may be specifically chloromethyleneiminium, and more specifically, 1-(chloromethylene)pyrrolidin-1-ium.

To achieve the above object, still another aspect of the present invention provides a method of preparing linear alpha-olefins (linear α -olefins), the method including the step of reacting a linear or cyclic alkene compound in the presence of the ruthenium complex catalyst.

In this regard, the ruthenium, complex catalyst and the linear alpha-olefin are the same as described above.

The method of preparing linear alpha-olefins is characterized in that the linear or cyclic alkene compound as a reactant is reacted using the ruthenium complex catalyst, and thus linear alpha-olefins may be obtained in a high yield.

The reaction may be an ethylene-metathesis ethenolysis reaction, but is not limited thereto.

Hereinafter, the present invention will be described in more detail with reference to Examples. However, these Examples are for illustrative purposes only, and the scope of the present invention is not intended to be limited by these Examples.

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Example 1: Preparation of Acyclic Carbene Ligand and Ruthenium Catalyst

Formamide was treated with oxalyl chloride, and then reacted with alkoxy silane to obtain an acyclic carbene ligand (L1-L12). The acyclic carbene ligand was subjected to a phosphine exchange reaction with a phosphine ruthenium catalyst to synthesize a novel ruthenium catalyst. Detailed procedures and reaction conditions for each step are described below.

Example 1-1: Preparation of Acyclic Carbene Ligand

Formamide (1 equiv.) was dissolved in dichloromethane (DCM), and then oxalyl chloride ((COCl)₂, 1.5 equiv.) was added dropwise to the solution at -78° C., and this mixture was heated to room temperature and stirred for 1 hr. After removing the solvent, the product was dissolved again in DCM, and a DCM solution of alkoxy silane (ROTMS, 1 equiv.) was added dropwise at -78° C., and this mixture was heated to room temperature and stirred for 4 hr. Thereafter, the mixture was recrystallized from hexane to obtain each ligand compound of L1 to L12.

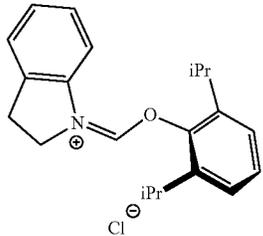
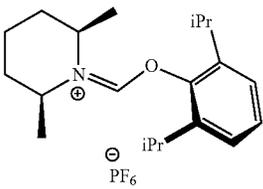
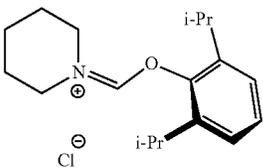
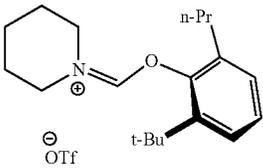
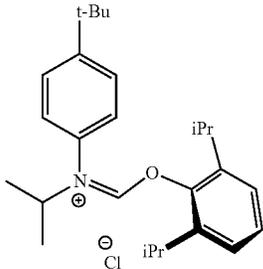
The obtained ligand compounds, L1 to L12, are as in Table 1 below.

TABLE 1

Ligand compound	Structural formula
L1	
L2	
L3	
L4	

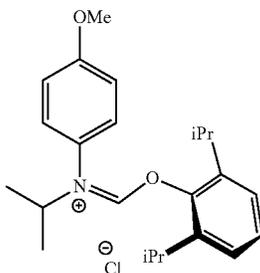
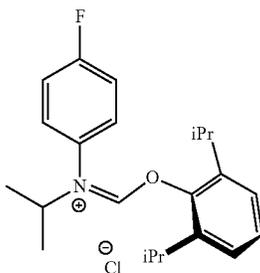
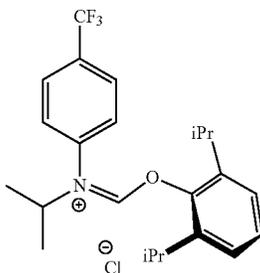
11

TABLE 1-continued

Ligand compound	Structural formula
L5	
L6	
L7	
L8	
L9	

12

TABLE 1-continued

Ligand compound	Structural formula
L10	
L11	
L12	

Example 1-2: Synthesis of Novel Ruthenium Catalyst

A novel ruthenium catalyst was synthesized using each of the ligand compounds. Each of the compounds L1 to L12 (2 equiv.) and a benzene solution of potassium bis(trimethylsilyl)amide (KHMDs, 2.2 eq.) were stirred at room temperature for 30 min. This solution was filtered and added to a benzene solution of a phosphine ruthenium catalyst. This mixture was filtered through a pad of Celite and extracted with benzene, and then the filtrate was concentrated. Thereafter, purification was performed by column chromatography, and each of the novel ruthenium catalyst compounds, Ru1 to Ru14, were obtained.

The compound names of the ruthenium catalyst compounds, Ru1 to Ru14, are shown in Tables 2 and 3.

TABLE 2

Compound	Name of compound
Ru1	Dichloro[(2,6-diisopropylphenoxy) (pyrrolidin-1-ium-1-ylidene)methanide] (2-isopropoxyphenylmethylene) ruthenium(II)
Ru2	Dichloro[(2,6-dibenzhydryl-4-methylphenoxy) (pyrrolidin-1-ium-1-ylidene)methanide] (2-isopropoxyphenylmethylene) ruthenium(II)
Ru3	Dichloro[(2-(tert-butyl)-6-propylphenoxy) (pyrrolidin-1-ium-1-ylidene)methanide] (2-isopropoxyphenylmethylene) ruthenium(II)
Ru6	Dichloro[(2,6-diisopropylphenoxy) (piperidin-1-ium-1-ylidene)methanide] (2-isopropoxyphenylmethylene) ruthenium(II)
Ru8	Dichloro[(2,6-diisopropylphenoxy) (pyrrolidin-1-ium-1-ylidene)methanide] (2-phenoxyphenylmethylene) ruthenium(II)

Compound	Name of compound
Ru9	Dichloro[(Z)-(2,6-diisopropylphenoxy) ((2R,6S)-2,6-dimethylpiperidin-1-ium-1-ylidene)methanide] (2-phenoxyphenylmethylene) ruthenium(II)
Ru10	Dichloro[(2,6-diisopropylphenoxy) (piperidin-1-ium-1-ylidene)methanide] (2-phenoxyphenylmethylene) ruthenium(II)
Ru11	Dichloro[N-((2,6-diisopropylphenoxy) methaneidylene)-N-isopropylbenzenaminium] (2-phenoxyphenylmethylene) ruthenium(II)
Ru12	Dichloro[4-(tert-butyl)-N-((2,6-diisopropylphenoxy) methaneidylene)-N-isopropylbenzenaminium] (2-phenoxyphenylmethylene) ruthenium(II)
Ru13	Dichloro[N-((2,6-diisopropylphenoxy)methaneidylene)-4-fluoro-N-isopropylbenzenaminium] (2-phenoxyphenylmethylene) ruthenium(II)
Ru14	Dichloro[N-((2,6-diisopropylphenoxy)methaneidylene)-N-isopropyl-4-methoxybenzenaminium] (2-phenoxyphenylmethylene) ruthenium(II)

TABLE 3

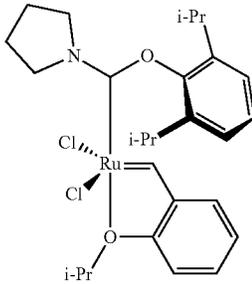
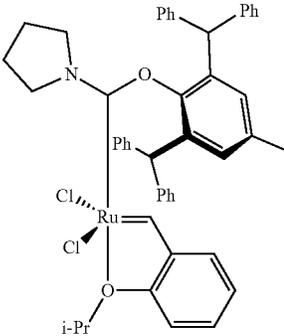
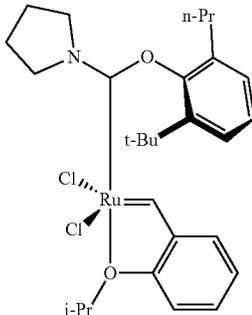
Compound	Structural formula	NMR	Yield
Ru1		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 15.69 (s, 1H), 7.59-7.50 (m, 1H), 7.50-7.41 (m, 1H), 7.30 (dd, $J = 7.7$ Hz, 2.7 Hz, 2H), 6.92 (dq, $J = 10.1$ Hz, 8.0 Hz, 3H), 5.15 (dt, $J = 9.7$ Hz, 6.0 Hz, 1H), 4.81 (dd, $J = 6.5$ Hz, 4.5 Hz, 2H), 4.04 (t, $J = 5.9$ Hz, 2H), 3.18 (td, $J = 11.0$ Hz, 6.7 Hz, 2H), 2.20 (dt, $J = 11.0$ Hz, 5.5 Hz, 2H), 2.06 (dd, $J = 12.5$ Hz, 7.1 Hz, 2H), 1.72 (dd, $J = 6.0$ Hz, 2.8 Hz, 6H), 1.12 (dd, $J = 6.8$ Hz, 2.8 Hz, 6H), 0.92 (dd, $J = 6.7$ Hz, 2.7 Hz, 6H).	51%
Ru2		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 16.33 (s, 1H), 7.67-7.59 (m, 1H), 7.16 (dd, $J = 10.1$ Hz, 4.6 Hz, 4H), 7.13-7.04 (m, 9H), 7.05-6.98 (m, 4H), 6.95 (t, $J = 7.4$ Hz, 1H), 6.86 (dd, $J = 7.5$ Hz, 1.6 Hz, 1H), 6.76 (dd, $J = 6.6$, 3.0 Hz, 4H), 6.58 (s, 2H), 5.90 (s, 2H), 4.64 (t, $J = 6.8$ Hz, 2H), 2.24 (s, 3H), 1.94 (p, $J = 6.8$ Hz, 2H), 1.80 (dd, $J = 12.9$ Hz, 6.8 Hz, 8H), 1.38 (p, $J = 6.9$ Hz, 2H).	62%
Ru3		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 15.91 (s, 1H), 7.60-7.46 (m, 2H), 7.36 (t, $J = 7.7$ Hz, 1H), 7.11 (dd, $J = 7.4$ Hz, 1.5 Hz, 1H), 7.06-6.88 (m, 3H), 5.19 (dt, $J = 12.3$ Hz, 6.1 Hz, 1H), 4.89 (tdd, $J = 17.0$ Hz, 10.0 Hz, 6.9 Hz, 2H), 4.12-3.93 (m, 2H), 2.64 (ddd, $J = 15.0$ Hz, 8.6 Hz, 6.6 Hz, 1H), 2.38-2.26 (m, 1H), 2.21 (qd, $J = 12.0$ Hz, 6.2 Hz, 2H), 2.11-2.00 (m, 2H), 1.76 (dd, $J = 6.1$ Hz, 1.7 Hz, 6H), 1.52-1.41 (m, 2H), 1.34 (s, 9H), 0.92-0.76 (m, 3H).	37%

TABLE 3-continued

Compound	Structural formula	NMR	Yield
Ru6		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 15.64 (d, $J = 16.0$ Hz, 1H), 7.58-7.50 (m, 1H), 7.49-7.42 (m, 1H), 7.29 (d, $J = 7.7$ Hz, 2H), 6.97-6.85 (m, 3H), 5.11 (dq, $J = 12.2$ Hz, 6.1 Hz, 1H), 4.57-4.45 (m, 2H), 4.07-3.96 (m, 2H), 3.18 (hept, $J = 6.9$ Hz, 2H), 2.15-2.03 (m, 2H), 1.85 (dt, $J = 11.8$ Hz, 5.7 Hz, 2H), 1.76-1.62 (m, 8H), 1.10 (d, $J = 6.9$ Hz, 6H), 0.94 (d, $J = 6.8$ Hz, 6H).	33%
Ru8		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 15.76 (d, $J = 11.4$ Hz, 1H), 7.54-7.39 (m, 6H), 7.39-7.31 (m, 3H), 7.02-6.95 (m, 2H), 6.63 (d, $J = 8.3$ Hz, 1H), 4.54 (t, $J = 6.6$ Hz, 2H), 4.02 (t, $J = 7.1$ Hz, 2H), 3.19 (dt, $J = 13.7$ Hz, 6.8 Hz, 2H), 2.14-1.93 (m, 4H), 1.14 (d, $J = 6.9$ Hz, 6H), 0.96 (d, $J = 6.8$ Hz, 6H).	18%
Ru9		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 15.79 (d, $J = 0.9$ Hz, 1H), 7.53-7.38 (m, 6H), 7.39-7.29 (m, 3H), 7.01-6.93 (m, 2H), 6.59 (d, $J = 8.3$ Hz, 1H), 5.10 (dd, $J = 14.9$ Hz, 10.7 Hz, 1H), 5.01-4.88 (m, 1H), 3.24 (dt, $J = 13.6$ Hz, 6.8 Hz, 1H), 3.12 (dt, $J = 13.6$ Hz, 6.8 Hz, 1H), 2.30 (td, $J = 12.8$ Hz, 6.6 Hz, 1H), 2.01 (dt, $J = 12.0$ Hz, 7.2 Hz, 1H), 1.90-1.77 (m, 1H), 1.75-1.56 (m, 6H), 1.41 (d, $J = 7.2$ Hz, 3H), 1.12 (dd, $J = 6.9$ Hz, 2.6 Hz, 6H), 0.98 (dd, $J = 6.8$ Hz, 3.3 Hz, 6H).	28%
Ru10		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 15.72 (d, $J = 13.8$ Hz, 1H), 7.51-7.40 (m, 6H), 7.37-7.31 (m, 3H), 6.98 (d, $J = 4.3$ Hz, 2H), 6.60 (d, $J = 8.3$ Hz, 1H), 4.30-4.14 (m, 2H), 4.05-3.93 (m, 2H), 3.19 (dt, $J = 13.7$ Hz, 6.8 Hz, 2H), 2.00-1.87 (m, 2H), 1.84-1.73 (m, 2H), 1.73-1.61 (m, 2H), 1.12 (d, $J = 6.9$ Hz, 6H), 0.98 (d, $J = 6.8$ Hz, 6H).	28%

TABLE 3-continued

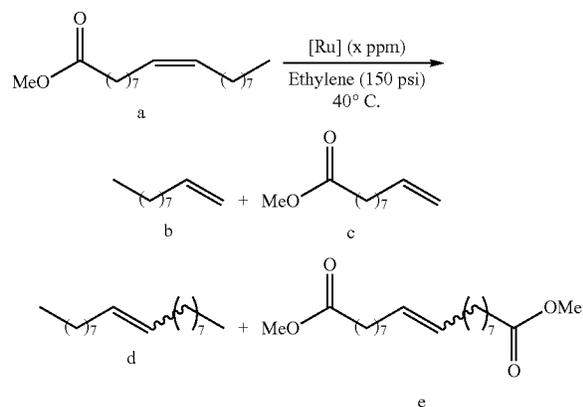
Compound	Structural formula	NMR	Yield
Ru11		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 15.70 (s, 1H), 53% 7.57-7.31 (m, 9H), 7.29-7.16 (m, 4H), 7.05-6.91 (m, 2H), 6.63 (d, J = 8.3 Hz, 1H), 5.14 (dt, J = 12.4 Hz, 6.2 Hz, 1H), 3.19 (dt, J = 13.6 Hz, 6.8 Hz, 2H), 1.45 (d, J = 6.3 Hz, 6H), 0.93 (dd, J = 40.0 Hz, 6.8 Hz, 12H).	
Ru12		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 15.75 (d, J = 43% 0.7 Hz, 1H), 7.59-7.33 (m, 7H), 7.28 (t, J = 13.8 Hz, 2H), 7.14 (t, J = 14.2 Hz, 2H), 7.05-6.91 (m, 2H), 6.63 (d, J = 8.3 Hz, 1H), 5.20-4.98 (m, 1H), 3.19 (dt, J = 13.4 Hz, 6.7 Hz, 2H), 1.44 (d, J = 6.2 Hz, 6H), 1.06-0.77 (m, 12H).	
Ru13		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 5.66 (d, J = 35% 0.7 Hz, 1H), 7.70-7.34 (m, 7H), 7.34- 7.06 (m, 6H), 7.06-6.93 (m, 2H), 6.66 (dd, J = 20.5 Hz, 8.5 Hz, 1H), 5.12 (dt, J = 12.5 Hz, 6.2 Hz, 1H), 3.16 (dt, J = 13.6 Hz, 6.8 Hz, 2H), 1.46 (t, J = 13.2 Hz, 6H), 1.14-0.79 (m, 12H).	

TABLE 3-continued

Compound	Structural formula	NMR	Yield
Ru14		¹ H NMR (400 MHz, CD ₂ Cl ₂) δ 15.72 (d, J = 43% 0.5 Hz, 1H), 7.58-7.29 (m, 9H), 7.26 (t, J = 6.6 Hz, 2H), 7.20-7.07 (m, 3H), 7.03-6.87 (m, 5H), 6.75-6.58 (m, 2H), 5.09 (dt, J = 12.4 Hz, 6.2 Hz, 1H), 3.77 (s, 3H), 3.18 (dt, J = 13.6 Hz, 6.8 Hz, 2H), 1.41 (t, J = 11.7 Hz, 6H), 1.01- 0.76 (m, 12H).	

Example 2. Measurement of Selectivity and Turnover Number of Ruthenium Catalyst Compound for Ethenolysis

The selectivity and the turnover number of each of the ruthenium catalyst compounds Ru1 to Ru14 prepared in Example 1 for an ethenolysis reaction were measured by the following methods.



In this regard,

Conversion was calculated as Conversion (%) = $\frac{1 - (\text{final number of moles of compound } a)}{(\text{initial number of moles of compound } a)} \times 100$,

Selectivity was calculated as Selectivity (%) = $\frac{(\text{Total number of moles of compounds } b \text{ and } c)}{[(\text{Total number of moles of compounds } b \text{ and } c) + (\text{Total number of moles of compounds } d \text{ and } e) \times 2]}$,

Yield was calculated as Yield (%) = $\frac{\text{Conversion} \times \text{Selectivity}}{100}$, and

Turnover number was calculated as Turnover number = $\frac{\text{Yield} \times (\text{initial number of moles of } a)}{\text{number of moles of catalyst}} / 100$.

The results are shown in Table 4 below.

TABLE 4

Ruthenium catalyst compound	Loading (ppm)	Conversion (%)	Selectivity (%)	Yield (%)	Turnover number
Ru1	50	80	90	72	14,000
	10	37	91	33	33,000
Ru2	50	51	89	45	9,000
	10	19	86	17	17,000
Ru3	50	86	91	73	16,000
	10	70	95	67	67,000
Ru4	5	52	97	50	100,0
	10	16	90	14	14,000
Ru5	50	4	93	4	800
Ru6	50	82	89	73	14,500
	10	5	88	4	4,000
Ru8	50	23	52	12	12,000
Ru9	50	45	84	37	7,500
Ru10	50	52	86	45	9,001
Ru11	50	55	84	46	9,200
Ru12	50	49	85	41	8,300
Ru13	50	48	87	42	8,400
Ru14	50	57	85	48	9,700

It was confirmed that the selectivity and turnover number of the prepared ruthenium catalyst compounds for the ethenolysis reaction were increased, and thus the yield of linear alpha-olefins was increased. In particular, it was confirmed that as the ring structure including the nitrogen atom of carbene was formed, the selectivity and turnover number were increased.

Comparative Example: Preparation of Acyclic Carbene Ligand and Ruthenium Catalyst

For comparison with the acyclic aminoxy carbene compounds, ruthenium catalyst compounds Ru15 and Ru16 were prepared by the method of Example 1-2, and the selectivity and turnover number of each compound for the ethenolysis reaction were measured.

The structure of each compound is shown in Table 5 below, and the selectivity and turnover number thereof are shown in Table 6.

TABLE 5

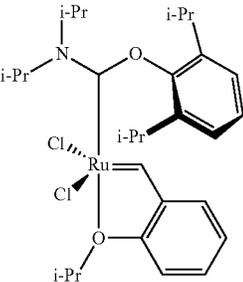
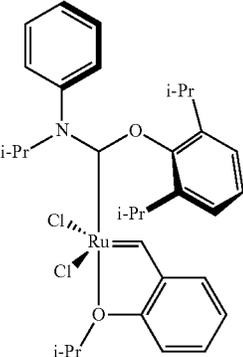
Compound	Structural formula	NMR	Yield
Ru15		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 15.64 (d, $J = 0.8$ Hz, 1H), 7.58-7.51 (m, 1H), 7.51-7.44 (m, 1H), 7.36-7.30 (m, 2H), 6.93 (t, $J = 6.7$ Hz, 1H), 6.90-6.86 (m, 2H), 5.25 (dt, $J = 12.4$ Hz, 6.2 Hz, 1H), 5.17-5.00 (m, 1H), 3.74 (hept, $J = 6.8$ Hz, 1H), 3.13 (hept, $J = 7.0$ Hz, 2H), 1.67 (dd, $J = 6.2$ Hz, 1.1 Hz, 12H), 1.54 (d, $J = 6.9$ Hz, 6H), 1.11 (d, $J = 6.9$ Hz, 6H), 0.86 (d, $J = 6.7$ Hz, 6H).	70%
Ru16		$^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 15.58 (d, $J = 0.6$ Hz, 1H), 7.62-7.53 (m, 1H), 7.47-7.33 (m, 4H), 7.29-7.17 (m, 4H), 6.99 (d, $J = 8.4$ Hz, 1H), 6.95-6.85 (m, 2H), 5.60-5.45 (m, 1H), 5.18 (dq, $J = 12.3$ Hz, 6.1 Hz, 1H), 3.18 (hept, $J = 6.9$ Hz, 2H), 1.74 (d, $J = 6.1$ Hz, 6H), 1.58 (d, $J = 6.3$ Hz, 6H), 0.89 (dd, $J = 35.9$ Hz, 6.8 Hz, 12H).	65%

TABLE 6

Ruthenium catalyst compound	Loading (ppm)	Conversion (%)	Selectivity (%)	Yield (%)	Turnover number
Ru15	50	1	92	1	230
Ru16	10	0.9	N.D.	0.9	900

As described above, it was confirmed that the catalyst compounds of the present invention showed remarkable selectivity and turnover number for the ethenolysis reaction, as compared with the ruthenium catalyst compound of Ru15 or Ru16.

Experimental Example: X-Ray Crystal Analysis

In order to investigate the solid-phase structure of the ruthenium catalyst single crystal by X-ray analysis, the structures of the ruthenium catalyst compounds Ru15 and Ru3 prepared in Example 2 and the Comparative Example were analyzed by X-ray crystallization. The results are shown in FIGS. 2A and 2B.

As a result, the selected bond length (\AA) and bond angle ($^\circ$) are as follows:

it was confirmed that the bond lengths and the bond angles of the ruthenium catalyst compound Ru15 were $\text{Ru—C1}=1.956(2)$ \AA , $\text{Ru—C20}=1.835(2)$ \AA , $\text{Ru—O1}=2.232(1)$ \AA , $\angle\text{N1—C1—O2}=109.5(1)^\circ$, $\angle\text{N1—C1—Ru}=117.0(1)^\circ$, and $\angle\text{Cl—Ru—Cl}=157.09(3)^\circ$ (FIG. 2A), and

the bond lengths and the bond angles of the ruthenium catalyst compound Ru3 were $\text{Ru—C11}=1.959(2)$ \AA ,

$\text{Ru—C1}=1.827(3)$ \AA , $\text{Ru—O1}=2.264(2)$ \AA , $\angle\text{N1—C11—O2}=108.0(2)^\circ$, $\angle\text{N1—C11—Ru}=117.0(2)^\circ$, and $\angle\text{Cl—Ru—Cl}=152.61(3)^\circ$ (FIG. 2B).

As a result, the ruthenium catalyst compounds Ru15 and Ru3 showed a distorted square-pyramidal structure, and had a structure in which the *lv*-aryl group is located, above O-benzylidene. In particular, it was confirmed that the angle of N—C—O was greater than that of the existing cyclic carbene N—C—N ($103\text{--}104^\circ$). Due to the increased angle, the acyclic carbene ligand of the present invention has excellent, electron-donating ability, and may help to improve selectivity due to the three-dimensional effect.

Based on the above description, it will be understood by those skilled in the art that the present disclosure may be implemented in a different specific form without changing the technical spirit or essential characteristics thereof. Therefore, it should be understood that the above embodiment is not limitative, but illustrative in all aspects. The scope of the disclosure is defined by the appended claims rather than by the description preceding them, and therefore all changes and modifications that fall within metes and bounds of the claims or equivalents of such metes and bounds are therefore intended to be embraced by the claims.

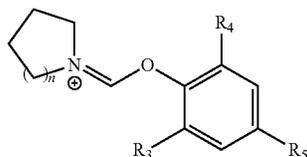
Effect of the Invention

An acyclic carbene ligand of the present invention and a ruthenium complex catalyst using the same have high selectivity and turnover number for terminal olefin formation in an ethylene-metathesis ethenolysis reaction, and thus linear α -olefins may be prepared with a high yield.

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What is claimed is:

1. An acyclic carbene ligand for the formation of a ruthenium complex, the acyclic carbene ligand having a structure of Chemical Formula 2:



[Chemical Formula 2]

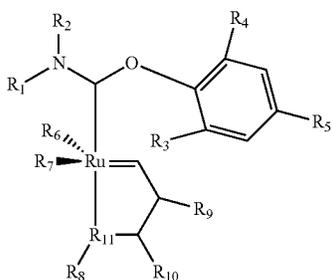
wherein, in Chemical Formula 2,
n is an integer of 0 to 4,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group, and

R₅ is a hydrogen atom or C₁-C₆ alkyl group.

2. The acyclic carbene ligand of claim 1, wherein n is an integer of 1 or 2, and R₃ and R₄ are each independently propyl, butyl, or diphenylmethyl.

3. A ruthenium complex catalyst having a structure of Chemical Formula 3:



[Chemical Formula 3]

wherein, in Chemical Formula 3,

R₁ and R₂ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group; or R₁ and R₂ are connected to each other to form an unsubstituted or substituted 4- to 8-membered heterocycle with a nitrogen atom to which they are connected,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group,

R₅ is a hydrogen atom or C₁-C₆ alkyl group,

R₆ and R₇ are each independently a halogen,

R₈ is a substituted or unsubstituted C₁-C₁₀ alkyl group, C₅-C₁₀ carbocycle, or 5- to 10-membered heterocycle,

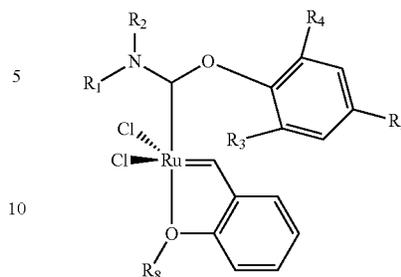
R₉ and R₁₀ are each independently a C₁-C₁₀ alkyl group, or are connected to each other to form a C₅-C₁₀ carbocycle or a 5- to 10-membered heterocycle, and

R₁₁ is N or O.

4. The ruthenium complex catalyst of claim 3, wherein the ruthenium complex catalyst has a structure of the following Chemical Formula 4:

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[Chemical Formula 4]



wherein, in Chemical Formula 4,

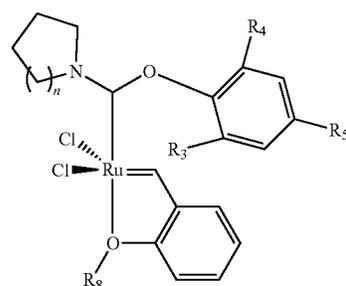
R₁ and R₂ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group; or R₁ and R₂ are connected to each other to form an unsubstituted or substituted 4- to 8-membered heterocycle with a nitrogen atom to which they are connected,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group,

R₅ is a hydrogen atom or C₁-C₆ alkyl group, and

R₈ is a substituted or unsubstituted C₁-C₁₀ alkyl group, C₅-C₁₀ carbocycle, or 5- to 10-membered heterocycle.

5. The ruthenium complex catalyst of claim 4, wherein the ruthenium complex catalyst has a structure of Chemical Formula 5:



[Chemical Formula 5]

wherein, in Chemical Formula 5,

n is an integer of 0 to 4,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group,

R₅ is a hydrogen atom or C₁-C₆ alkyl group, and

R₈ is a substituted or unsubstituted C₁-C₁₀ alkyl group, C₅-C₁₀ carbocycle, or 5- to 10-membered heterocycle.

6. The ruthenium complex catalyst of claim 5, wherein n is an integer of 1 or 2, and

R₃ and R₄ are each independently propyl, butyl, or diphenylmethyl.

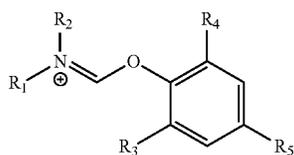
7. A method of using the ruthenium complex of claim 3 as a catalyst in an ethylene-metathesis ethenolysis reaction of a linear or cyclic alkene compound.

8. A method of preparing a ruthenium complex catalyst, the method comprising the steps of:
treating formamide with oxalyl chloride to obtain an intermediate;

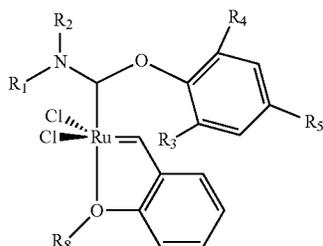
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reacting the intermediate with alkoxy silane to obtain an acyclic carbene ligand having a structure of Chemical Formula 1; and

binding the ligand with ruthenium to form a ruthenium complex catalyst having a structure of Chemical Formula 4:



[Chemical Formula 1]



[Chemical Formula 4]

wherein, in the above Chemical Formulae,

R₁ and R₂ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group; or R₁ and R₂ are connected to each other to form an unsubstituted or substituted 4- to 8-membered heterocycle with a nitrogen atom to which they are connected,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group,

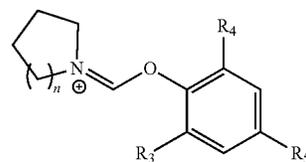
R₅ is a hydrogen atom or C₁-C₆ alkyl group, and

R₈ is a substituted or unsubstituted C₁-C₁₀ alkyl, C₅-C₁₀ carbocycle, or 5- to 10-membered heterocycle.

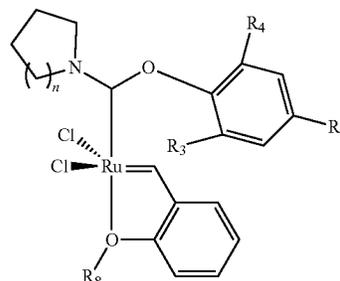
9. The method of claim 8, wherein the step of obtaining the ligand is a step of obtaining an acyclic carbene ligand having a structure of Chemical Formula 2, and the step of

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forming the ruthenium complex catalyst is a step of forming a ruthenium complex catalyst having a structure of Chemical Formula 5:



[Chemical Formula 2]



[Chemical Formula 5]

wherein, in the above Chemical Formulae,

n is an integer of 0 to 4,

R₃ and R₄ are each independently a hydrogen atom, a substituted or unsubstituted C₁-C₆ alkyl group, C₁-C₆ alkenyl group, C₁-C₆ alkynyl group, C₃-C₈ cycloalkyl group, or C₆-C₁₀ aryl group,

R₅ is a hydrogen atom or C₁-C₆ alkyl group, and

R₈ is a substituted or unsubstituted C₁-C₁₀ alkyl, C₅-C₁₀ carbocycle, or 5- to 10-membered heterocycle.

10. The method of claim 8, wherein the step of binding the ligand with ruthenium to form a ruthenium complex catalyst is a step of forming a ruthenium complex catalyst via a phosphine exchange reaction with a phosphine ruthenium catalyst.

11. A method of preparing linear alpha-olefins, the method comprising the step of reacting a linear or cyclic alkene compound in the presence of the ruthenium complex catalyst of claim 3.

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